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Patents ADP number (if you know it) 8531808002

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4. Title of the invention
TUNGSTEN BASED CATALYST SYSTEM
5. Name of your agent (if you have one)
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TUNGSTEN BASED CATALYST SYSTEM

FIELD OF THE INVENTION

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This invention relates to a catalyst system and to the use thereof in the dimerisation of olefins.

10 BACKGROUND ART

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Catalyst systems based on tungsten and aluminium activators are described in US 3,784,629; US 3,784,630; US 3,784,631; US 3,813,453; US 3,897,512; US 3,903,193 and J. Org. Chem., 1975, 40, 2983 – 2985. The use of such catalyst systems in the dimerisation of light olefins is also known.

20

US 5,059,739 describes a catalyst system for olefin dimerisation and codimerisation prepared *in situ* by the reaction of a tungsten precursor with an aniline ligand in a 1:1 molar ratio at reflux in chlorobenzene under a flow of an inert gas to remove HCl evolved from the system. After completion of this reaction an aluminium activator was added to the mixture. The resulting catalyst system was used in the dimerisation and codimerisation of butene and lighter olefins.

25

J. Mol. Cat. A., Chem, 1999, 148, 43-48 also discloses a catalyst system with a tungsten to aniline ligand ratio of 1 to 1. The catalyst system was used to dimerise light olefins in the form of propene and ethene.

The present inventors have now developed a novel catalyst system which is distinguished over the prior art in that a different tungsten to ligand molar ratio is used in combination with the removal or neutralisation of acid formed by the reaction of a ligand precursor and a source of tungsten. This catalyst system is particularly suitable for use in the dimerisation of olefins and it has also been found that the catalyst influences the regioselectivity of the reaction.

DISCLOSURE OF THE INVENTION

10

According to a first aspect of the present invention there is provided a catalyst system including the combination of

- a source of tungsten;
- a ligand precursor containing at least N or O as a bonding atom to bond to the tungsten in the source of tungsten, the source of tungsten and the ligand precursor being selected to form an acid due to the bonding of the ligand precursor to the tungsten;

15

and the catalyst system being characterized therein that it is substantially free of the acid formed due to the bonding of the ligand precursor to tungsten; and that the molar ratio of the source of tungsten to ligand precursor is at least $1: 3/n$ where n is the number of bonds that the ligand precursor forms with the tungsten.

20



Acid free

The acid formed due to the bonding of the ligand precursor to the tungsten may be removed or neutralised in any suitable manner. Where the formed acid
5 comprises HCl it may be removed by an inert gas stream as described in US 5,059,739 which is incorporated herein by reference.

In a preferred embodiment of the invention the formed acid is neutralised by the addition of a base. Accordingly the catalyst system may comprise a
10 combination of the said source of tungsten; said ligand precursor; and a base.

The base may comprise any suitable base for neutralising the acid formed. The base may comprise a Brønsted base. A Brønsted base will be understood to be a base as defined by J. N. Brønsted, Recl. Trav. Chim. Pays-Bas, 1923, 42,
15 718 – 728 and T. M. Lowry, Chem. Ind. London, 1923, 42 and 43. The base may be an organic base, preferably an amine, preferably a tertiary amine, preferably triethylamine.

The base may comprise aniline or a substituted aniline, but preferably the base
20 is selected not to react with the source of tungsten.

The amount of the base to be added will depend on the type of ligand precursor and more particularly the amount of acid produced by the reaction of the ligand precursor with the source of tungsten. Preferably sufficient base is added to

- neutralise substantially all the acid formed. Preferably the molar ratio of the base: ligand precursor is at least 1 (m/p) : 1, where m is the molar amount of acid produced due to the reaction of 1 mole of ligand precursor with 1 mole of the source of tungsten, and p is the molar amount of acid formed neutralised by 1 mole of base. Preferably said base: ligand molar ratio is from 1(m/p) : 1 to 20 (m/p): 1; preferably from 1 (m/p) : 1 to 2 (m/p) : 1.

Ratio of source of tungsten to ligand precursor:

- As stated above the molar ratio of the source of tungsten to ligand precursor is at least 1 : 3/n, where n is the number of bonds that the ligand precursor forms with the tungsten. Preferably said molar ratio is at least 1 : 4/n and preferably it is not higher than 1 : 5/n. In a preferred embodiment of the invention the said ratio is about 1 : 4/n. For example with WCl_6 as the source of tungsten and with aniline ($PhNH_2$) as the ligand precursor the source of tungsten to ligand precursor is preferably 1 : 2 as aniline forms a double bond with the tungsten in WCl_6 .

- It will be appreciated that the present invention is not limited to any specific compound formed due to the reaction between the source of tungsten and the ligand precursor and n is the expected number of bonds to form between the source of tungsten and the ligand precursor. It is believed that the species $L_nWL'_2$ is preferably formed due to the combination of the tungsten source with the ligand precursor, where L is the ligand from the ligand precursor and L' is

any group which would leave the complex when reacted with an activator or displaced by an olefinic moiety.

Source of tungsten:

5

The source of tungsten may comprise any suitable source of tungsten, preferably with the tungsten in the 6⁺ oxidation state. The source of tungsten may comprise an organic salt, an inorganic salt or an organometallic complex.

- 10 Preferably the source of tungsten comprises a salt, preferably a salt of the formula WX_n , where X is any suitable anion (X being the same or different where $n > 1$) and $n = 1-6$. Preferably X is selected from halide, oxo, amide anion, organyl (including alkyl and aryl), $-O-(\text{organyl})$ (including alkoxy) or OTf (trifluoromethanesulfonyl), methanesulfonyl, OTos (*p*-toluenesulphonyl).
- 15 Preferably the source of tungsten is a tungsten halide, preferably a tungsten chloride, preferably WCl_6 .

The ligand precursor:

- 20 In a preferred embodiment of the invention the ligand precursor may include only N and/or O as bonding atoms to bond to the tungsten. In one embodiment of the invention the ligand precursor may include only two such bonding atoms which may be the same or different in which case the ligand precursor may define a bidentate ligand. In an alternative embodiment of the invention the

ligand precursor may include a single such bonding atom in which case the ligand precursor may form a monodentate ligand.

5 The bonding atoms of the ligand precursor may be electron donating atoms to form a coordination compound with the source of tungsten.

The ligand precursor may be selected from the group consisting of a carboxylic acid; an alcohol; a diketone; and an amine. Preferably it comprises an amine.

10 The ligand precursor preferably includes an aromatic or heteroaromatic moiety, preferably an aromatic moiety.

The ligand precursor may comprise a bidentate ligand precursor such as an aromatic or heteroaromatic bidentate ligand precursor said bidentate ligand precursor may for example comprise a substituted or non-substituted
15 diaminonaphthalene, such as 1,8-diaminonaphthalene. Alternatively the bidentate ligand precursor may be selected from the group consisting of H_2NANH_2 , $\text{R}'(\text{H})\text{NANH}_2$, $\text{R}'(\text{H})\text{NAN}(\text{H})\text{R}''$, H_2NAOH , $\text{R}'(\text{H})\text{NAOH}$, HOAOH , $\text{HOA}=\text{O}$ and $\text{O}=\text{A}=\text{O}$, where A is a bond or a bridging group of one to 10 spacer atoms, and
20 R' and R'' are independently an organic moiety, preferably an organyl group, preferably an aromatic group.

Preferably the ligand precursor comprises a monodentate ligand precursor, preferably a compound of the formula $\text{R}^1\text{NH}_{3-q}$, wherein q is from 1-2 and R^1 is

an organic moiety, preferably an organyl group and R^1 being the same or different when $q=2$. Preferably at least one R^1 group is an aromatic compound. The ligand precursor may comprise an aromatic amine such as aniline or a substituted aniline.

5

Mixtures of different monodentate ligand precursors may be used, as may mixtures of different bidentate ligand precursors or mixtures of monodentate and bidentate ligand precursors.

10 Activator

The catalyst systems may also include an activator of the catalyst system. These activators may be reducing agents.

15 In one embodiment of the invention the activator may comprise a compound containing a Group 3A atom, and preferably the Group 3A atom is Al or B.

Aluminium compounds that may be suitable are compounds such as $R_n^2AlX_{3-n}$, wherein $n = 0$ to 3 ; wherein X is halide; and wherein R^2 is an organic moiety, R^2 being the same or different when $n > 1$, and preferably R^2 is independently an organyl group (including alkyl, aryl); an oxygen containing moiety (such as alkoxy or aryloxy). Examples include trimethylaluminium (TMA), triethylaluminium (TEA), tri-isobutylaluminium (TIBA), tri-n-octylaluminium, methylaluminium dichloride, ethylaluminium dichloride, dimethylaluminium

20

chloride, diethylaluminium chloride, aluminium isopropoxide, ethylaluminiumsesquichloride, methylaluminium-sesquichloride, and aluminoxanes. Aluminoxanes are well known in the art as typically oligomeric compounds which can be prepared by the controlled addition of water to an alkylaluminium compound (for example trimethylaluminium, to give methylaluminoxane (MAO) or triethylaluminium to give ethylaluminoxane (EAO). Such compounds can be linear, cyclic, cages or mixtures thereof. Mixtures of different aluminoxanes may also be used in the process.

- 10 It should be noted that aluminoxanes generally also contain considerable quantities of the corresponding trialkylaluminium compounds used in their preparation. The presence of these trialkylaluminium compounds in aluminoxanes can be attributed to their incomplete hydrolysis with water. Any quantity of a trialkylaluminium compound quoted in this disclosure is additional to alkylaluminium compounds contained within the aluminoxanes.
- 15

The activator may be selected from alkylaluminoxanes such as methylaluminoxane (MAO) and ethylaluminoxane (EAO) as well as modified alkylaluminoxanes such as modified methylaluminoxane (MMAO). Modified methylaluminoxane (a commercial product from Akzo Nobel) contains modifier groups such as isobutyl groups, in addition to methyl groups. However in one preferred embodiment the activator comprises ethylaluminium dichloride.

20

Examples of suitable boron activator compounds are boroxines, NaBH_4 , triethylborane, *tris*(pentafluorophenyl)borane, lithium *tetrakis*(pentafluorophenyl) borate, ammonium and etheral borate salts (e.g. $[\{\text{Et}_2\text{O}\}_2\text{H}][\text{B}(\text{C}_6\text{F}_5)_4]$, $[\text{Ph}_2\text{MeNH}][\text{B}(\text{C}_6\text{F}_5)_4]$), tributyl borate and the like.

5

The activator may also be or contain a further compound that acts as a reducing agent, such as sodium or zinc metal and the like. Other activators that can be used include alkyl or aryl zinc and lithium reagents.

- 10 The source of tungsten and the activator may be combined in molar ratios of Al:W or B:W from about 3:5:1 to 1000:1, preferably from about 4:1 to 50:1, and more preferably from 5:1 to 25:1.

Method

15

The invention also relates to a method of preparing a catalyst system comprising the steps of combining

- a source of tungsten;
 - a ligand precursor containing at least N or O as a bonding atom to bond to
- 20 the tungsten in the source of tungsten, the source of tungsten and the ligand precursor being selected to form an acid due to the bonding of the ligand precursor to the tungsten;

wherein the molar ratio of the source of tungsten to ligand precursor is at least 1: 3/n, where n is the number of bonds that the ligand precursor forms with the

tungsten; and the method including the step of removal or neutralisation of acid formed due to the bonding of the ligand precursor to the tungsten.

Preferably the said formed acid is neutralised by the addition of a base.

5

Preferably the process also includes the step of adding an activator for activating the catalyst system.

The source of tungsten, ligand precursor and base may be combined in any
10 order and preferably thereafter the activator is added.

The components of the catalyst system may be thoroughly mixed, preferably at a temperature from 0 to 200°C.

15 The invention also relates to a catalyst system prepared by the method as set out above.

Catalyst system applications:

20 According to another aspect of the present invention there is provided the use of the catalyst system substantially as herein described to dimerise or codimerise compounds containing an olefinic moiety.

It has been found that the catalyst system is particularly useful to prepare a

mono-methyl branched dimerised product (especially a mono branched mono methyl branched dimerised product) especially of α -olefins including α -olefins with five or more carbon atoms. It has also been found that this catalyst system influences the regioselectivity of dimerisation reactions.

5

Accordingly to another aspect of the present invention there is provided a process for the dimerisation of a starting compound or different of starting compounds, each starting compound including an olefinic moiety, the process comprising the steps of mixing at least one starting compound with a catalyst system substantially as described herein above to form a dimerised product of a starting compound or a codimerised product of different starting compounds.

10

The catalyst system may be pre-prepared, but preferably the catalyst system is formed *in situ* during mixing with the at least one starting compound.

15

Each starting compound preferably includes an α -olefinic moiety and preferably each starting compound comprises an α -olefin. In one embodiment of the invention an α -olefin of five or more carbon atoms is dimerised, preferably the starting olefin has only one double bond between carbon atoms and in one embodiment of the invention the starting olefin is 1-hexene.

20

Preferably only a single branch is formed due to the dimersation, and preferably this branch is a methyl branch. In a preferred embodiment of the invention the starting compound is dimerised to a mono branched, preferably a mono-methyl

branched dimerisation product. Preferably the starting compound is linear. In the case where 1-hexene is the starting compound the dimerisation product may be 5-methylundecenes (mixture of isomers in terms of position of unsaturation). In a preferred embodiment of the invention the reaction produces a reaction product containing more than 50wt% of the mono branched mono-methyl product, preferably more than 65wt%. Preferably the reaction is regioselective to form a mono branched mono-methyl dimerisation product of the starting compound.

10

The process may be carried out in a solvent. The solvent may be part of the starting compound(s) but preferably the solvent is an inert solvent which does not react with the catalyst system. Such an inert solvent may for example comprise benzene, toluene, chlorobenzene, xylene, cumene, tert-butylbenzene, sec-butylbenzene, heptane, methylcyclohexane, methylcyclopentane, cyclohexane, ionic liquid and the like.

The process may be carried out at temperatures from -20°C to 200°C . It will be appreciated that the choice of solvent and starting compound may determine a suitable temperature range for the process. Temperatures in the range of $50 - 150^{\circ}\text{C}$ are preferred.

The starting compound may be contacted with the catalyst system at any pressure.

According to another aspect of the present invention there is provided a dimerised product or co-dimerised product produced by the process substantially as described hereinabove.

5

EXAMPLES

The invention will now be further described by means of the following non-limiting examples.

10

Example 1

A stirred reaction vessel (dried under vacuum at elevated temperature and back-filled with inert gas [Ar or N₂]) was charged with a source of tungsten in the form of WCl₆ (0.1 mmol), chlorobenzene solvent (10 ml), nonane (standard), Et₃N (0.4 mmol) as a base, PhNH₂ (0.2 mmol) as ligand precursor and 1-hexene as a starting olefinic compound (100 mmol) and heated to 60°C for 15 minutes. The catalysis was then initiated by addition of ethylaluminium dichloride (EADC) (1.1 mmol), and the vessel stirred at 60°C for 4 hours.

20

The run was terminated by addition of 2ml of a MeOH/H₂O (50:1) solution and stirring for 5 minutes. Subsequently, distilled water (50 ml) was added and the mixture vigorously stirred, then allowed to separate and the organic layer separated and filtered. The organic layer was analysed by GC. An activity of 107.2 (mol 1-C₆) (mol M)⁻¹ hr⁻¹ with a TON of 428.7 (mol 1-C₆) (mol M)⁻¹ was

calculated for this experiment. The product composition of the reaction mixture at the end of the test (in terms of hydrocarbon fractions) was C₁₂ (87.8wt%), C₁₈, (1.3wt%) and heavies, [C₂₄] (10.9wt%).

The skeletal selectivity (determined after hydrogenation of the olefinic dimer product – see Example 4) within the C₁₂ (dimer) fraction is: linear product 0%; mono-methylbranched product (as 5-methylundecenes) 65%; di-methylbranched product (as 5,6-dimethyldecenes) 35%.

It was found that when the base triethylenediamine (DABCOTM) was used as a base instead of Et₃N under the same conditions as in this example the results achieved were less favourable.

Table 1. Selectivity within the dimer (C₁₂) fraction observed for example 1 – GC trace data.

Retention Time	Relative Peak Area
19.93	5.84
20.05	1346.19
20.13	91.83
20.32	19.55
20.44	194.62
20.52	176.15
20.56	84.40
20.60	6.95
20.65	72.28
20.79	1064.97
20.89	9.46
20.94	9.43
21.09	2.70
21.17	4.05
21.48	2.49

Example 2

The representative procedure described in example 1 was used, except 4-fluoroaniline (0.2 mmol) was used in place of aniline.

5

The product composition of the reaction mixture at the end of the test (in terms of hydrocarbon fractions) was C₁₂ (94.0wt%), C₁₈, (1.2wt%) and heavies, [C₂₄] (4.8wt%).

10 **Table 2.** Selectivity within the dimer (C₁₂) fraction observed for example 2.

Retention Time	Relative Peak Area
19.89	2.11
19.92	2.76
20.05	1356.01
20.13	104.40
20.31	19.02
20.44	183.01
20.52	153.25
20.55	104.00
20.60	6.89
20.64	72.32
20.79	1275.17
20.89	7.00
20.93	6.71
21.03	1.64
21.17	4.52
21.48	3.60

Example 3

15

The representative procedure described in example 1 was used, except *p*-toluidine (0.2 mmol) was used in place of aniline.

The product composition of the reaction mixture at the end of the test (in terms of hydrocarbon fractions) was C₁₂ (66.8wt%), C₁₈, (0.0wt%) and heavies, [C₂₄] (33.2wt%).

5

Table 3. Selectivity within the dimer (C₁₂) fraction observed for example 3.

Retention Time	Relative Peak Area
19.04	2.29
20.02	273.31
20.11	24.00
20.30	3.49
20.42	16.87
20.54	41.79
20.62	9.95
20.76	281.43

Example 4

10

The representative procedure described in example 1 was used, except 1,8-diaminonaphthalene (0.1 mmol) was used in place of aniline.

15 The product composition of the reaction mixture at the end of the test (in terms of hydrocarbon fractions) was C₁₂ (10.1wt%), C₁₈, (0.0wt%) and heavies, [C₂₄] (89.9wt%).

Table 4. Selectivity within the dimer (C₁₂) fraction observed for example 4.

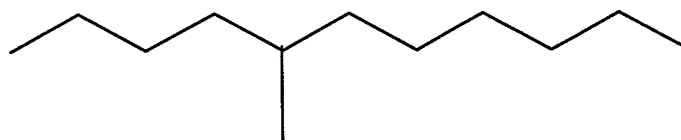
20

Retention Time	Relative Peak Area
20.02	2.15
20.75	3.66

Example 5

A sample of the organic layer recovered from example 1 was reduced under vacuum to leave the dimerised olefinic product as essentially the main component (traces of chlorobenzene and nonane persisted). This was then hydrogenated using Pd/C (Degussa type E1002 XU/W, 0.5 g of 5% Pd/C per 100 mmol of olefin moiety) under H₂ (1 bar), 8 hours. The solution was filtered and GC analysis obtained.

- 10 The GC + ¹³C NMR analysis showed that a single major paraffinic product resulted from hydrogenation namely 5-methyl-undecane:



The paraffinic product was also analysed by ¹³C {¹H} pendant NMR spectroscopy. The chemical shifts observed agree with those predicted by theory for 5-methyl-undecane.

